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(54) An oxide fluorescent glass capable of exhibiting visible fluorescence

(57) A glass material which is capable of exhibiting fluorescence in the visible region by ultraviolet ray excitation is represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

SiO_2	2 to 60 %,
B_2O_3	5 to 70 % (SiO_2 + B_2O_2 = 50 to 70 %)
RO	5 to 30 % (R: at least one atom selected from Mg, Ca, Sr and Ba)

ZnO	0 to 15 %
ZrO_2	0 to 10 %,
Tb_2O_3 or Eu_2O_3	2 to 15 % (containing either Tb_2O_3 or Eu_2O_3)
Ln_2O_3	0 to 20 % (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Sm, Dy and Tm)

CeO_2	0 to 1 %
Bi_2O_3	0 to 2 %
Sb_2O_3	0.01 to 0.5 % and
R'_2O	0 to 20 % (R': at least one atom selected from Li, Na and K)

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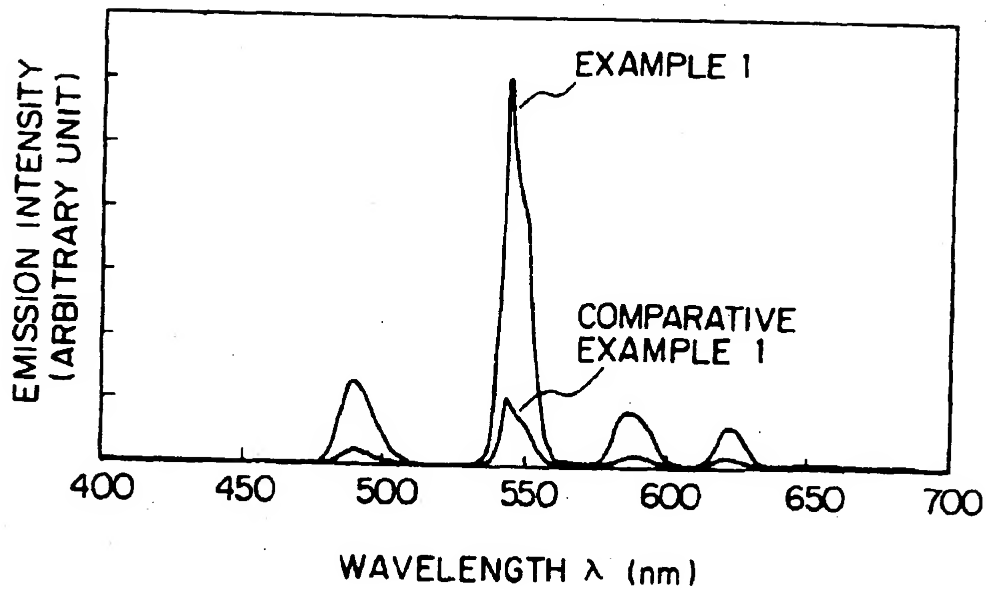
FIG. 1


EMISSION INTENSITY (ARBITRARY UNIT)
EXAMPLE 1
COMPARATIVE EXAMPLE 1
400
450
500
550
600
650
700
WAVELENGTH λ (nm)

Description

This invention relates to a material for converting an invisible ultra-violet ray into a visually observable visible ray with high efficiency, and is concerned with an oxide fluorescent glass capable of exhibiting visible fluorescence, which is useful for controlling an optical axis of a laser beam such as an excimer laser and can be applied to fluorescent tubes for lamps, fluorescent fibers, backlights or LED display devices.

Phosphors using rare earth elements have been used widely up to the present time, mainly, as phosphors for lamps, color picture tubes, etc. Of late materials for the anti-Stokes-wise wavelength conversion of infrared light into visible light have extensively been studied, for example, as to application to laser materials.

The Tb ion showing a green fluorescence has been put to practical use in color picture tubes, high color rendering fluorescent lamps, etc. The Eu ion showing a fluorescence with a narrow spectrum width in the red region has been put to use in color picture tubes, high color rendering fluorescent lamps, etc. As described above, a phosphor using Tb or Eu has already been put to practical use, but such a phosphor is an opaque material which is obtained by coating a suitable carrier with a powdered phosphor to thus give only a superficial omission.

As a glass utilizing the fluorescence of Tb or Eu, there have been used those described in Japanese Patent Publication No. 27047/1982 and 27048/1982 and Japanese Patent Laid-Open Publication No. 133780/1996.

However, the glasses described in these publications, for example, in Japanese Patent Publication No. 27047/1982 contain only at most 1.5 mol % of Eu_2O_2 as a fluorescent agent. In the case of Japanese Patent Publication No. 27048/1982, only at most 1.5 mol % of Tb_2O_2 is contained as a fluorescent agent. In such a degree of concentration of Eu_2O_3 or Tb_2O_3, insufficient fluorescent intensity is obtained. In the case of Japanese Patent laid-Open Publication No. 133780/1996, a large amount of the fluorescent agent is included, but a fluorophosphate is used and thus, production of a glass for a fluorescent lamp or large-sized glass plate is difficult due to its low heat tolerance and low glass strength.

It is an object of the present invention to provide a Tb- or Eu-containing oxide fluorescent glass whereby the above described problems of the prior art can be solved.

It is another object of the present invention to provide a Tb- or Eu-containing oxide fluorescent glass in which a large quantity of Tb or Eu can be incorporated, concentration quenching is restrained and a strong fluorescence is exhibited in the visible region by irradiation of ultraviolet rays such as an excimer laser, and which has excellent thermal durability as well as high glass strength.

These objects can be attained by an oxide fluorescent glass capable of exhibiting fluorescence in the visible region by excitation with ultra-violet rays, having a chemical composition comprising, at least, silicon (Si), boron (B) and oxygen (O), and further containing terbium (Tb) or europium (Eu) as a fluorescent agent.

The accompanying drawings illustrate the principle and merits of the present invention.

Fig. 1 is a graph showing a fluorescent spectrum glass prepared in Example 1 with Comparative Example 1, excited by an ultraviolet ray of 365 nm.

Fig. 2 is a graph showing a fluorescent spectrum of the glass prepared in Example 6, excited by an ultraviolet ray of 365 nm.

Generally, the fluorescence of rare earth ions tends to be subject to concentration quenching and the basic absorption of a glass matrix at the short wavelength side is shifted to the long wavelength side with increase in amounts of rare earth elements. Accordingly, capture of excited energy takes place by the non-emission center, so that a fluorescent material presenting a strong fluorescence cannot be obtained. This problem can first be solved by the present invention. Furthermore, thermal durability or glass strength can be improved by the use of an oxide glass according to the present invention.

That is, according to the present invention, there is provided (1) an oxide fluorescent glass capable of exhibiting fluorescence in the visible region by excitation with ultraviolet rays, having a chemical composition comprising, at least, silicon (Si), boron (B) and oxygen (O), and further containing terbium (Tb) or europium (Eu) as a fluorescent agent.

Specifically, the present invention relates to (2) an oxide fluorescent glass capable of exhibiting visible flurescence, as described in the above (1), which is represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

SiO_2	2 to 60 %,
B_2O_3	5 to 70 % (SiO_2 + B_2O_3 = 50 to 70 %)
RO	5 to 30 % (R: at least one atom selected from Mg, Ca, Sr and Ba)
ZnO	0 to 15 %
ZrO_2	0 to 10 %,
Tb_2O_3	or Eu_2O_3 2 to 15 % (containing either Tb_2O_3 or Eu_2O_3)

(continued)

Ln_2O_3	0 to 20 % (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Sm, Dy and Tm)
CeO_2	0 to 1 %
Bi_2O_3	0 to 2 %
Sb_2O_3	0.01 to 0.5 % and
R'_2O	0 to 20 % (R': at least one atom selected from Li, Na and K)

The reasons for limiting the composition range of each component of this oxide fluorescent glass to that described above are as follows:

SiO_2 is a glass-forming component, which is present in a proportion of 2 to 60 %, since if less than the lower limit, the viscosity of the glass melt is too low to form the glass, while if more than the upper limit, the melting temperature is too high to prepare the glass. The preferred range is 5 to 50 %.

B_2O_3 is a glass-forming component, which is present in a proportion of 5 to 70 %, since if less than the lower limit, it is difficult to form the glass, while if more than the upper limit, durability is deteriorated. The preferred range is 10 to 60 %.

The sum of SiO_2 + B_2O_3 should be 50 to 70 %, preferably 50 to 65 %.

RO (R: at least one atom selected from Mg, Ca, Sr and Ba), Zn and Zr are components for improving the melting properties of the glass, which are present in proportions of RO 5 to 30 %, ZnO 0 to 15 % and ZrO_2 0 to 10 %, since if more than the upper limit, the glass is unstable and tends to be crystallized, while if less than the lower limit, the glass is difficult to melt. The preferred ranges are RO 15 to 25 %, ZnO 0 to 10 % and ZrO_2 0 to 4 %. Large amounts of Tb_2O_3 or Eu_2O_3 can be stably incorporated in the glass by incorporating RO (alkaline metal earth oxides) as an essential component.

R'_2O (R': at least one atom selected from Li, Na and K) acts to lower the melting temperature of a glass melt, which is present in a proportion of 0 to 20 %, since if exceeding the above described range, the water resistance is raised and the tendency to devitrification is increased, thus rendering the glass unstable. The preferred range is 0 to 15 %.

Tb_2O_3 is an important component capable of presenting green fluorescence by ultraviolet excitation. This component should be present in a proportion of 2 to 15 %, since if more than the upper limit, the glass is difficult to obtain. The preferred range is 2.1 to 11.3 %.

Eu_2O_3 is an important component capable of presenting red fluorescence by ultraviolet excitation. This component should be present in a proportion of 2 to 15 %, since if more than the upper limit, the glass is hard to obtain The preferred range is 2.3 to 11.7 %.

Ln_2O_3 (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Sm, Dy and Tm) is a component for increasing the viscosity of the glass and suppressing crystallization. This component should be present in a proportion of 0 to 20 %, since if more than the above described range, the above described effect is deteriorated. The preferred range is 0 to 10 %.

CeO_2 is a component acting as a sensitizer of Tb, which is present in a proportion of 0 to 1 %, but if exceeding the above described upper limit, this effect is decreased. In addition, this is also a component for exhibiting blue fluorescence when not containing Tb. The preferred range is 0 to 0.2 %.

Bi_2O_3 is a component acting as a sensitizer of Eu, which is present in a proportion of 0 to 2 %, but if exceeding the above described upper limit, the percent transmission of ultraviolet rays is lowered and this effect is decreased. The preferred range is 0 to 1 %.

Sb_2O_3 is a component acting as a cleaning agent, which is present in a proportion of 0.01 to 0.5 %, but if exceeding the above described upper limit, the percent transmission of ultraviolet rays is lowered, while if less than the lower limit, this effect is decreased. The preferred range is 0.02 to 0.2 %.

Production of the oxide fluorescent glass capable of exhibiting visible fluorescence, according to the present invention is carried out by mixing the corresponding raw material compounds to a proportion of the object composition, for example, silica, boric anhydride, zinc oxide, calcium carbonate, terbium oxide, europium oxide, etc., melting the resulting mixture in the air at a temperature of 1200 to 1500 °C for 2 to 3 hours and allowing the mixture to flow out into a metallic mold, followed by shaping.

Preferred embodiments of the present invention are described below:

(I) An oxide fluorescent glass capable of exhibiting visible fluorescence, as described in the foregoing (1), which is represented, in term of atoms for making up the glass, by a chemical composition (mol %) shown in Table 1:

Table 1

SiO_2	5 to 50 %

Table 1 (continued)

B_2O_3	10 to 60 %
$SiO_2 + B_2O_3$	50 to 70 %
RO①	15 to 25 %
ZnO	0 to 10 %
ZrO_2	0 to 4 %
R'_2O②	0 to 15 %
$Tb_2O_3$④	2.1 to 11.3 %
$Eu_2O_3$④	2.3 to 11.7 %
$Ln_2O_3$③	0 to 10 %
CeO_2	0 to 0.2 %
Bi_2O_3	0 to 1 %
Sb_2O_3	0.02 to 0.2 %

(Note)
①R: at least one atom selected from Mg, Ca, Sr and Ba
②R': at least one atom selected from Li, Na and K
③Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Sm, Dy and Tm)
④either Tb_2O_3 or Eu_2O_3

The present invention will now be illustrated in detail without limiting the same:

Example 1

Raw materials were mixed according to the weight ratios of Example No. 1 shown in Table 2 to give a composition of Example No. 1 shown in Table 3. In this case, CaO and BaO were given from the corresponding carbonates or nitrates. The thus prepared raw materials were melted at a temperature of 1200 to 1500 °C for 2 to 3 hours, allowed to flow into a metallic mold and shaped to a glass in stable manner.

When the resulting glass was excited by an ultraviolet ray of 365 nm, green fluorescence was exhibited to give a fluorescent spectrum shown in Fig. 1.

Examples 2 to 5

Raw materials were mixed according to the weight ratios of the Example Nos. shown in Table 2 and melted in a similar manner to Example 1 to obtain glass compositions shown in Table 3 in stable manner.

When the resulting glasses in Examples 2 to 5 were excited by an ultra-violet ray of 365 nm, similar spectra to Example 1 were obtained exhibiting green fluorescence.

Example 6

Raw materials were mixed according to the weight ratios of Example No. 6 shown in Table 2 to give a composition of Example No. 6 shown in Table 3. In this case, BaO and Na_2O were given from the corresponding carbonates or nitrates. The thus prepared raw materials were melted at a temperature of 1200 to 1500 °C for 2 to 3 hours, allowed to flow into a metallic mold and shaped to obtain a glass in stable manner.

When the resulting glass was excited by an ultraviolet ray of 365 nm, red fluorescence was exhibited to give a fluorescent spectrum shown in Fig. 2.

Examples 7 to 10

Raw materials were mixed according to weight ratios of the Example Nos. shown in Table 2 and melted in the similar manner to Example 6 to obtain glass compositions shown in Table 3 in stable manner.

When the resulting glasses in Examples 7 to 10 were excited by an ultra-violet ray of 365 nm, similar spectra to Example 6 were obtained exhibiting red fluorescence.

Table 2

(g)

Example No.	1	2	3	4	5	6	7	8	9	10
SiO_2	6.0	3.0	8.4	10.4	32.0	32.0	32.0	23.0	10.4	6.0
B_2O_3	37.0	40.0	35.2	33.2	8.0	8.0	8.0	31.0	33.2	37.0
CaO	10.0	10.0	12.6	12.6				14.3	12.6	10.0
BaO					32.0	32.0	32.0			
ZnO	5.0	5.0	3.8	2.0	8.0	8.0	8.0		2.0	5.0
ZrO_2					5.0		5.0			
Na_2O					5.0	5.0	5.0	7.9		
Tb_2O_3	15.0	15.0	15.0	41.8	8.5					
Eu_2O_3						13.0	10.0	17.9	41.8	8.0
La_2O_3	27.0	27.0	20.0							20.0
Gd_2O_3			5.0		1.5					14.0
CeO_2	0.1	0.1	0.1		0.1					
Bi_2O_3						2.0		5.9		
Sb_2O_3	0.1	0.05	0.05	0.2	0.1	0.2	0.1	0.2	0.2	0.2

Table 3

(mol %)

Example No.	1	2	3	4	5	6	7	8	9	10
SiO_2	10.0	5.1	13.5	17.1	48.2	49.5	48.2	30.0	17.0	10.0
B_2O_3	53.4	58.1	48.9	47.0	10.4	10.7	10.4	35.0	46.8	53.4
CaO	17.9	18.0	21.7	22.2				20.0	22.1	17.9
BaO					18.9	19.4	18.9			
ZnO	6.2	6.2	4.5	2.4	8.9	9.1	8.9		2.4	6.2
ZrO_2					3.7		3.7			
Na_2O					7.3	7.5	7.3	10.0		
Tb_2O_3	4.1	4.2	4.0	11.3	2.1					
Eu_2O_3						3.4	2.6	4.0	11.7	2.3
La_2O_3	8.3	8.4	5.9							6.2
Gd_2O_3			1.3		0.4					3.9
CeO_2	0.06	0.06	0.06		0.05					
Bi_2O_3						0.4		1.0		
Sb_2O_3	0.03	0.02	0.02	0.07	0.03	0.06	0.03	0.05	0.07	0.07

Comparative Example 1

Raw materials were mixed in a weight ratio calculated from a glass composition known in the art, i.e. 75 % of B_2O_3, 17 % of Na_2O, 2 % of Al_2O_3, 3.45 % of CaO, 1 % of La_2O_3, 0.05 % of Eu_2O_3 and 1.5 % of Tb_2O_3 (by mol %), melted at a temperature of 1000 to 2000 °C for 2 to 3 hours, allowed to flow into a metallic mold and shaped to obtain a glass in stable manner. In this case, the amount of Eu or Tb is less than in the Examples of the present invention.

When the resulting glass was excited by an ultraviolet ray of 365 nm and a fluroescence spectrum was measured, a similar spectrum to Example 1 was obtained exhibiting green fluorescence. However, the emission intensity was given as the highest peak at 542 nm, corresponding to 1/3 times of that of Example 1, as shown in Fig. 1.

Advantages of the Invention

The oxide fluorescent glass of the present invention is capable of converting an invisible ultraviolet ray into a visually observable visible ray with a high efficiency and available for controlling an optical axis of a laser beam such

as an excimer laser. In addition, the fluorescent glass of the present invention can be applied to fluorescent tubes for lamps, fluorescent fibers, backlights or LCD display devices, so it is expected that industrial applications of the present invention will be enlarged.

Claims

1. An oxide fluorescent glass capable of exhibiting fluorescence in the visible radiation region by excitation with ultraviolet rays, having a chemical composition comprising, at least, silicon, boron and oxygen, and further containing terbium or europium as a fluorescent agent.

2. The oxide fluorescent glass capable of exhibiting visible flurescence, as claimed in Claim 1, which is represented, in term of atoms for making up the glass, by the following chemical composition (mol %):

SiO_2	2 to 60 %,
B_2O_3	5 to 70 % ($SiO_2 + B_2O_3$ = 50 to 70 %)
RO	5 to 30 % (R: at least one atom selected from Mg, Ca, Sr and Ba)
ZnO	0 to 15 %
ZrO_2	0 to 10 %,
Tb_2O_3 or Eu_2O_3	2 to 15 % (containing either Tb_2O_3 or Eu_2O_3)
Ln_2O_3	0 to 20 % (Ln: at least one atom selected from Y, La, Gd, Yb, Lu, Sm, Dy and Tm)
CeO_2	0 to 1 %
Bi_2O_3	0 to 2 %
Sb_2O_3	0.01 to 0.5 % and
R'_2O	0 to 20 % (R': at least one atom selected from Li, Na and K)

3. Use of an oxide fluorescent glass as claimed in claim 1 or claim 2 in controlling the axis of a laser beam, in fluorescent tubes for lamps, fluorescent fibers, backlights and LCD display devices.

FIG. 1

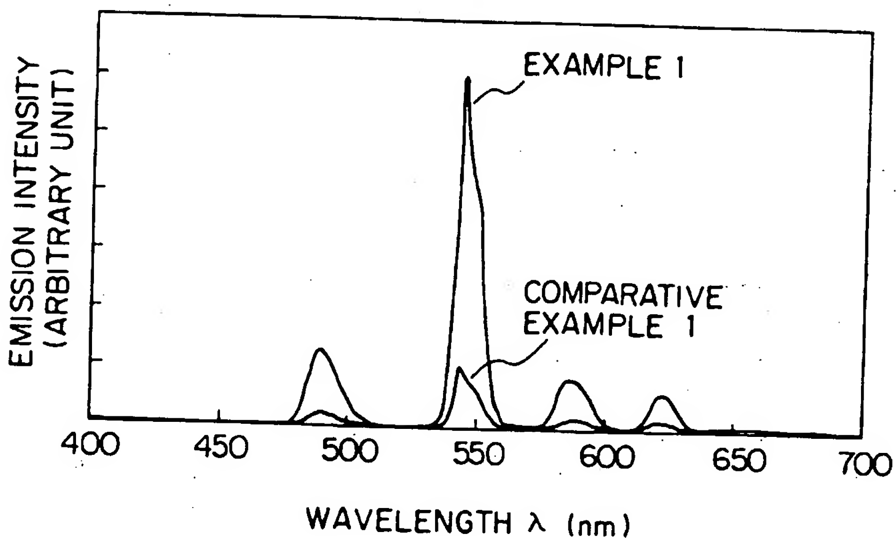
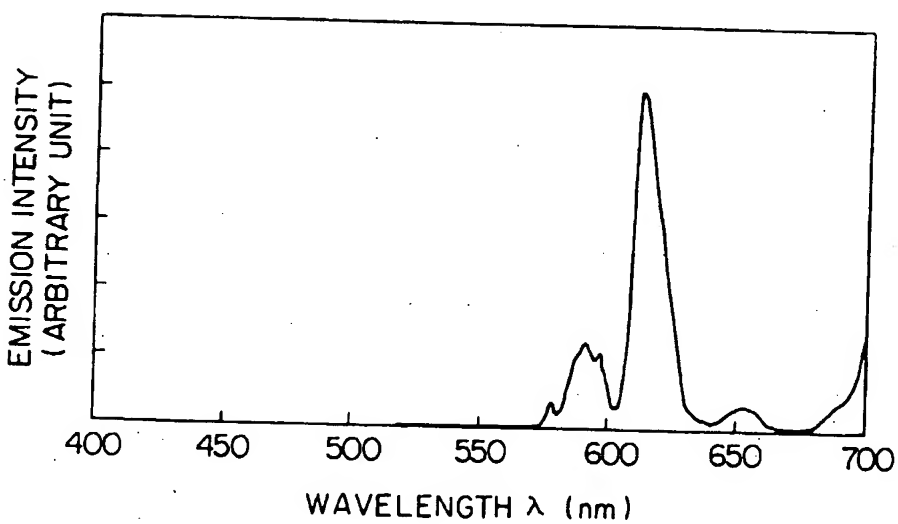

EXAMPLE 1
COMPARATIVE EXAMPLE 1
EMISSION INTENSITY (ARBITRARY UNIT)
400
450
500
550
600
650
700
WAVELENGTH λ (nm)

FIG. 2


EMISSION INTENSITY (ARBITRARY UNIT)
400
450
500
550
600
650
700
WAVELENGTH λ (nm)

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 9979

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 338 934 A (CENTRE NAT RECH SCIENT) * claims; figure 1 * ---	1-3	C03C3/068 C03C3/095 C03C4/12
X	US 5 039 631 A (KRASHKEVICH DAVID ET AL) * column 2, line 19 - line 47 * * claims; tables * ---	1-3	
X	US 5 108 959 A (BUCHANAN ROBERT A ET AL) * column 1, line 54 - line 29 * * column 3, line 11 - line 64 * * claims; table 1 * ---	1-3	
X	EP 0 266 812 A (PHILIPS NV) * claims; examples * ---	1	
A	GB 1 136 239 A (SYLVANIA ELEC PRODUCTS INC) * the whole document * ---	1-3	
A	DATABASE WPI Section Ch, Week 7535 Derwent Publications Ltd., London, GB; Class L01, AN 75-57668W XP002058455 & JP 49 116 111 A (SUWA SEIKOSHA KK) , 6 November 1974 * abstract * ---	1-3	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C03C
A	DATABASE WPI Section Ch, Week 8305 Derwent Publications Ltd., London, GB; Class L01, AN 83-10494K XP002058456 & JP 57 205 339 A (HITACHI LTD) , 16 December 1982 * abstract * --- -/--	1-3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	10 March 1998	Kuehne, H-C

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 9979

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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D,A	DATABASE WPI Section Ch, Week 7515 Derwent Publications Ltd., London, GB; Class L03, AN 75-24919W XP002058458 & JP 49 099 610 A (SANTOKU METAL IND CO LTD) , 20 September 1974 * abstract * ---	1-3	
A	EP 0 709 345 A (SUMITA OPTICAL GLASS) * the whole document *	1-3	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D	& JP 08 133 780 A -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	10 March 1998	Kuehne, H-C

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